

tion, followed by drying under vacuum overnight. The product was dissolved in diethyl ether and recrystallized to remove any residual ammonia. The diethyl ether was then removed by rotary evaporation, followed by drying under vacuum overnight.  $\text{NH}_3\text{BH}_3$  (9.82 g) was recovered as a microcrystalline powder (0.318 mol, 98% yield). Purity of the product was based on XRD and  $^{11}\text{B}$  NMR results.  $^1\text{H}$  NMR d-glyme showed a slight triplet at 3.8 ppm ( $\text{NH}_3$ ,  $J_{N-H}=45$  Hz) and a 1:1:1:1 quartet centered at 1.5 ppm ( $\text{BH}_3$ ,  $J_{B-H}=94$  Hz).  $^{11}\text{B}$  NMR showed a quartet -23 ppm ( $\text{BH}_3$ ,  $J_{B-H}=93$  Hz).

TABLE 2 compares results from the syntheses detailed in Examples 1-5.

TABLE 2

Reactants and conditions for Synthesis of Ammonia Borane (AB) in accordance with the invention.						
SYNTHESIS	BH SOURCE	NH SOURCE	AMMONIA BOROHYDRIDE ( $\text{NH}_4\text{BH}_4$ ) (MOLARITY IN $\text{NH}_3$ )	AMMONIA BORANE ( $\text{NH}_3\text{BH}_3$ ) (MOLARITY IN THF)	SOLVENT	YIELD AB (%)
1	$\text{NaBH}_4$	$\text{NH}_4\text{Cl}$	0.74	0.20	$\text{NH}_3/\text{THF}^*$	99
2	$\text{NaBH}_4$	$\text{NH}_4\text{Cl}$	1.90	0.20	$\text{NH}_3/\text{THF}^*$	99
3	$\text{NaBH}_4$	$\text{NH}_4\text{Cl}$	1.90	0.20	$\text{NH}_3/\text{THF}$	99
4	$\text{LiBH}_4\text{:THF}^{**}$	$\text{NH}_4\text{F}$	0.74	0.18	$\text{NH}_3/\text{THF}$	99
5	$\text{NaBH}_4$	$\text{NH}_4\text{Cl}$	3.10	2.56	$\text{NH}_3/\text{THF}$ (15.5° C.; 100 psia $\text{NH}_3$ )	98

\* $\text{NH}_4\text{BH}_4$  was isolated and  $\text{NH}_3$  removed prior to addition of THF solvent in these experiments.

\*\*Lithium borohydride salt was acquired in THF solvent and used without modification.

In the table, near-quantitative yields of AB were obtained under various reaction conditions. Results are described further hereafter.

In synthesis 1 (sequential addition, Example 1), AB was formed at a near quantitative yield. A borohydride salt was mixed with an ammonium salt in liquid ammonia to form solid ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ). A mixture of NaCl and ammonium borohydride (including any complexed  $\text{NH}_3$ ) was recovered (isolated) from liquid ammonia solvent as a polycrystalline solid. Addition of THF to the solid containing  $\text{NH}_4\text{BH}_4$  produced AB at a near quantitative yield. Low salt concentrations were used. These experiments demonstrated: 1) that the DADB formation pathway is not critical, and 2) decomposition of ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ) to DADB does not occur when liquid ammonia is present at a concentration greater than about 10 wt %, a surprising result.

In synthesis 2 (sequential addition, Example 2), a borohydride salt was mixed with an ammonium salt in liquid ammonia to form solid ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ). A mixture of NaCl and ammonium borohydride (including any complexed  $\text{NH}_3$ ) was again isolated from liquid ammonia solvent as a polycrystalline solid. Addition of THF to the solid containing  $\text{NH}_4\text{BH}_4$  produced AB at a near quantitative yield. Results demonstrate that not only is the DADB formation pathway not required, dilute concentrations of reactant salts are not required, another surprising result. Use of concentrated reactant salts will assist industrial-scale production of AB. And, again, undesirable side reactions including, e.g., decomposition of ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ) to DADB, is controlled when liquid ammonia is present at a concentration >10 wt %. Finally, results demonstrate that complete removal of ammonia in the reaction synthesis is not required.

In synthesis 3 (parallel addition, Example 3), a borohydride salt was mixed with an ammonium salt simultaneously

(i.e., in parallel) in liquid ammonia to form solid ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ). Addition of THF to  $\text{NH}_4\text{BH}_4$  solid in liquid ammonia produced AB at a near quantitative yield. This experiment demonstrates the feasibility of simultaneous reaction processing; one or more reactants can be added to the solvent phase in parallel. Results demonstrate that the ether-based solvent (e.g., THF) does not have to be added only after the metathesis reaction has happened. It can be added at any time during the reaction sequence, e.g., while the ammonia solvent ( $\text{NH}_3$ ) is still present.

In synthesis 4 (parallel addition, Example 4), feasibility of complex parallel processing was demonstrated. In this

experiment, a borohydride salt ( $\text{LiBH}_4$ ) that was premixed in THF (the secondary) solvent was added simultaneously (i.e., in parallel) to liquid ammonia solvent containing a different ammonium salt ( $\text{NH}_4\text{F}$ ). Results demonstrated a near-quantitative yield of AB, a very surprising result given previous literature reports. Need for solid reactants, dilute reactant conditions (i.e., high solvent concentrations), and an absence of  $\text{NH}_3$  are not required. Further, near-quantitative yields can be obtained from complex mixtures of various reactants. In addition, the secondary (ether-based) solvent can be added simultaneously.

In synthesis 5 (parallel addition, Example 5), a borohydride salt was mixed with an ammonium salt simultaneously (i.e., in parallel) under a positive partial pressure of  $\text{NH}_3$  (about 100 psia) that allowed the salts to be mixed at a higher temperature (15.5° C.) in a liquid ammonia solvent. Addition of THF produced AB at a near quantitative yield. Results demonstrate that low reaction temperatures are not required, an additional finding demonstrating the advantages and utility of the processes of the present invention. Presence of the liquid ammonia solvent prevents side reactions such as formation of DADB and other unwanted polymeric products such as PAB that would be expected to lower the yield of AB product. Results indicate that formation of DADB is eliminated by the present invention. Findings further show that a yield of AB product can be obtained in ether and ammonia/THF solvent mixtures at concentrations 2.5 times those reported in the research literature, a new finding.

What is claimed is:

1. A method for preparing ammonia borane, characterized by the steps of:

reacting a preselected quantity of a borohydride salt with an ammonium salt in liquid ammonia at a preselected temperature and pressure to form ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ); and